Development and Evaluation of a Novel Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO_2 Capture

Yongqi Lu[1], Xinhuai Ye[1], Manoranjan Sahu[1], Massoud Rostam-Abadi[1,2], Andrew Jones[3]

[1]Illinois State Geological Survey, University of Illinois at Urbana-Champaign;
[2] Dept. of Environmental Eng., University of Illinois at Urbana-Champaign;
[3] U.S. Department of Energy, National Energy Technology Laboratory

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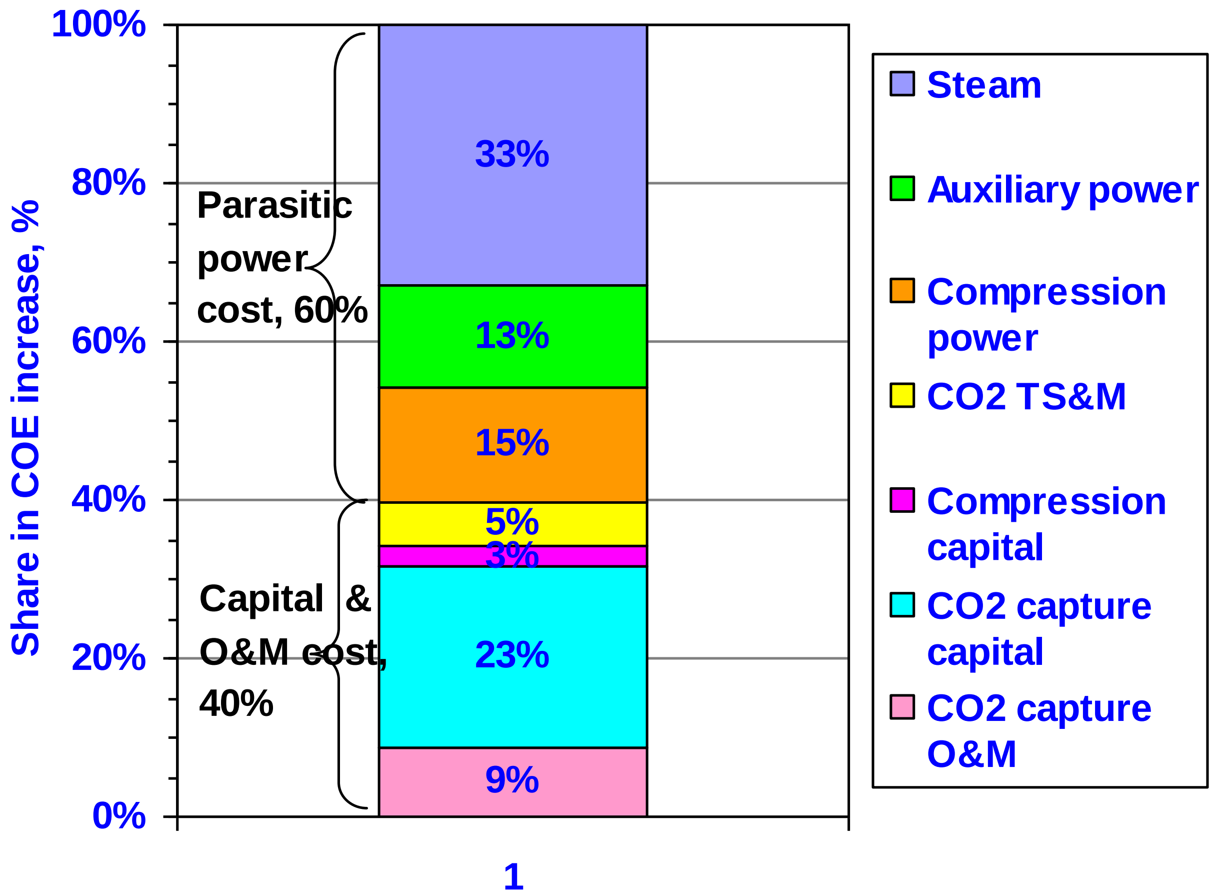
Cost Breakdown of Benchmark MEA Process

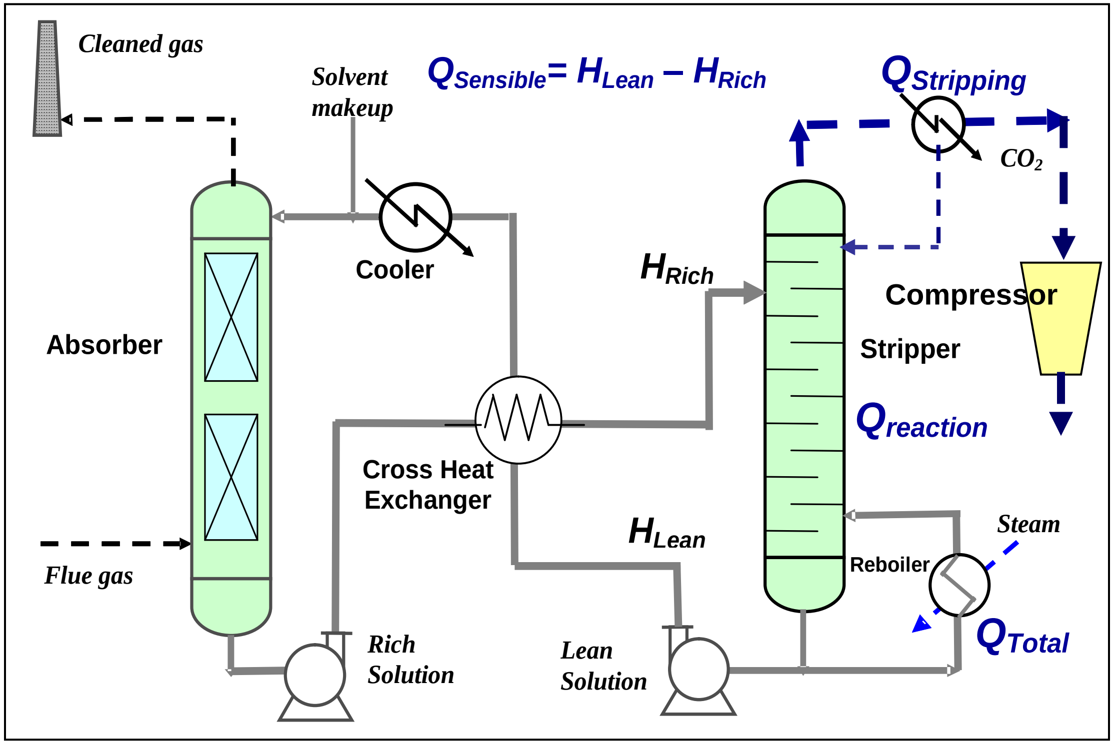
- Benchmark MEA process
  - 86% increase in Cost of Electricity (COE)
  - 60% of total cost contributed by parasitic power loss



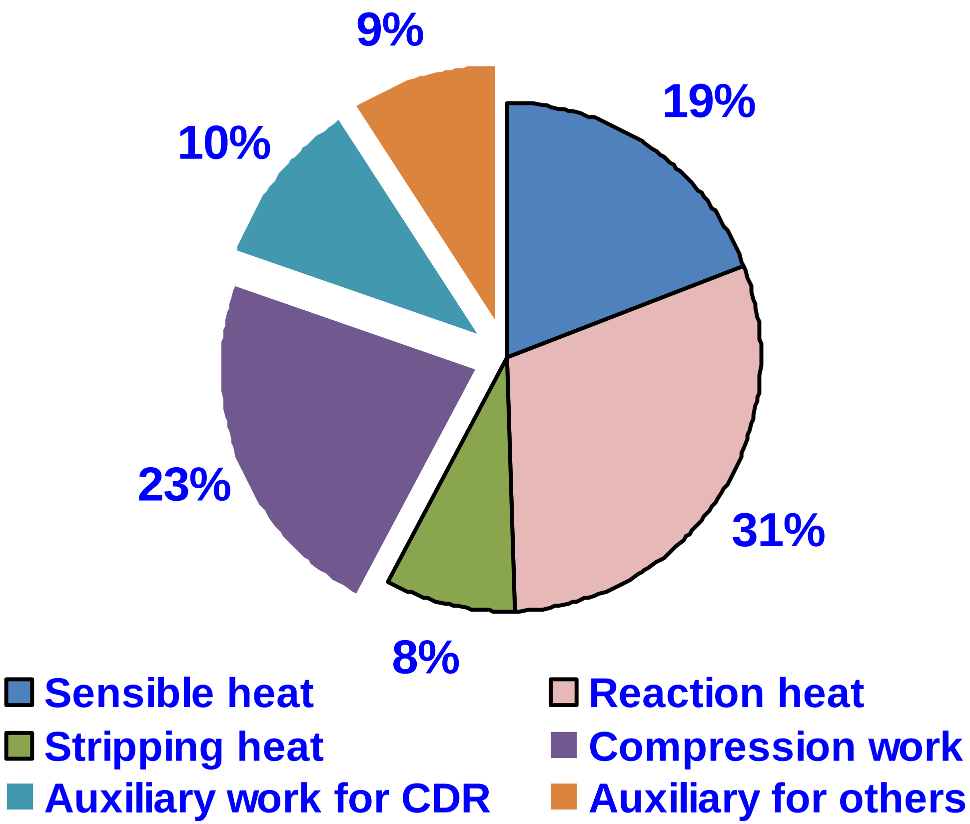
Parasitic Power Consumption of Absorption-Based Process

Energy use components

- CO_2 desorption (steam use)
  - Heat of absorption (rxn heat)
  - Sensible heat (heat for ΔT between CO_2-rich and lean solvents)
  - Stripping heat (water vaporization)
- CO_2 compression work
- Auxiliary work
  - Work for CDR
  - Others



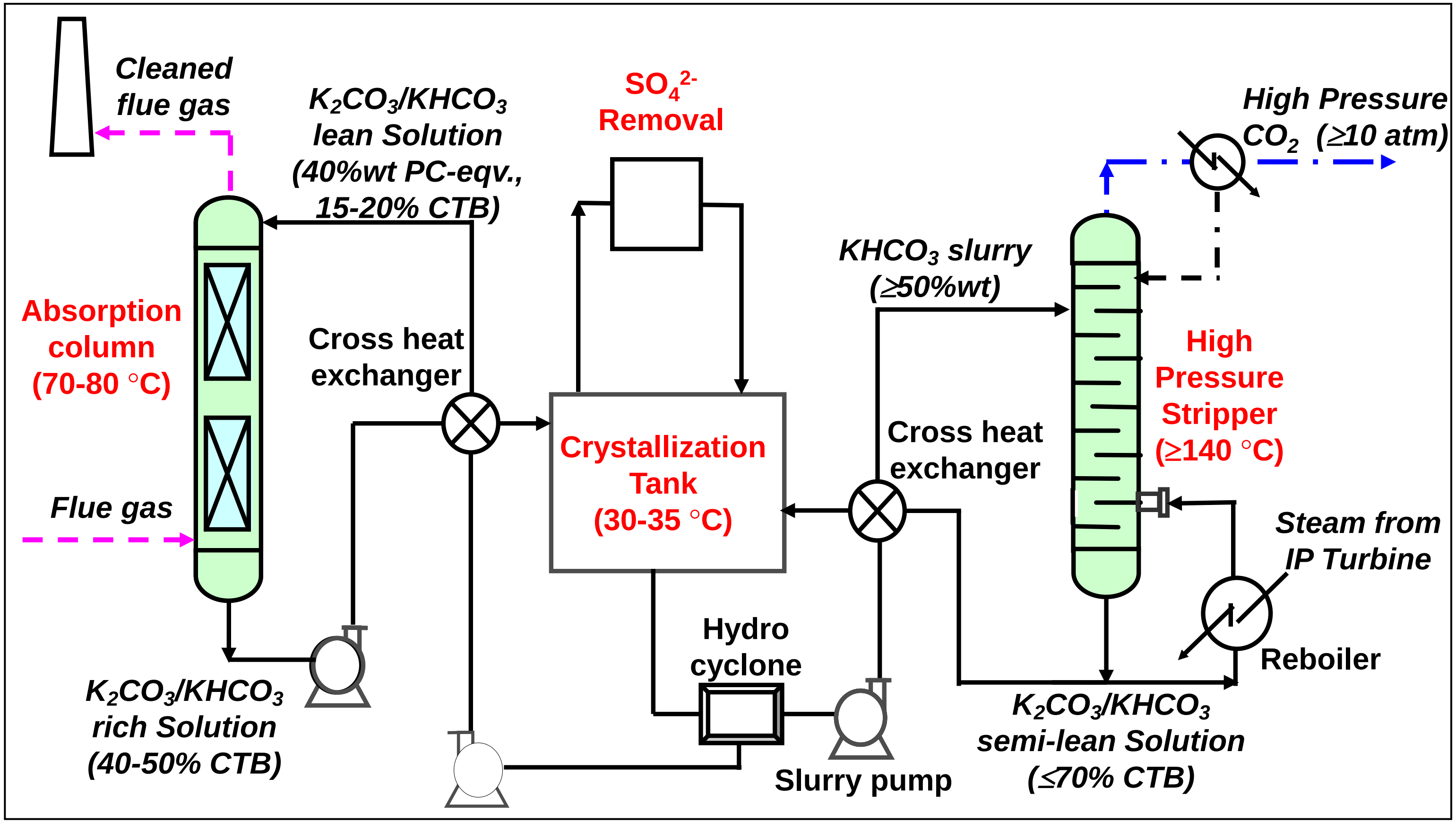
Energy use Breakdown of Benchmark MEA Process



Energy intensive:

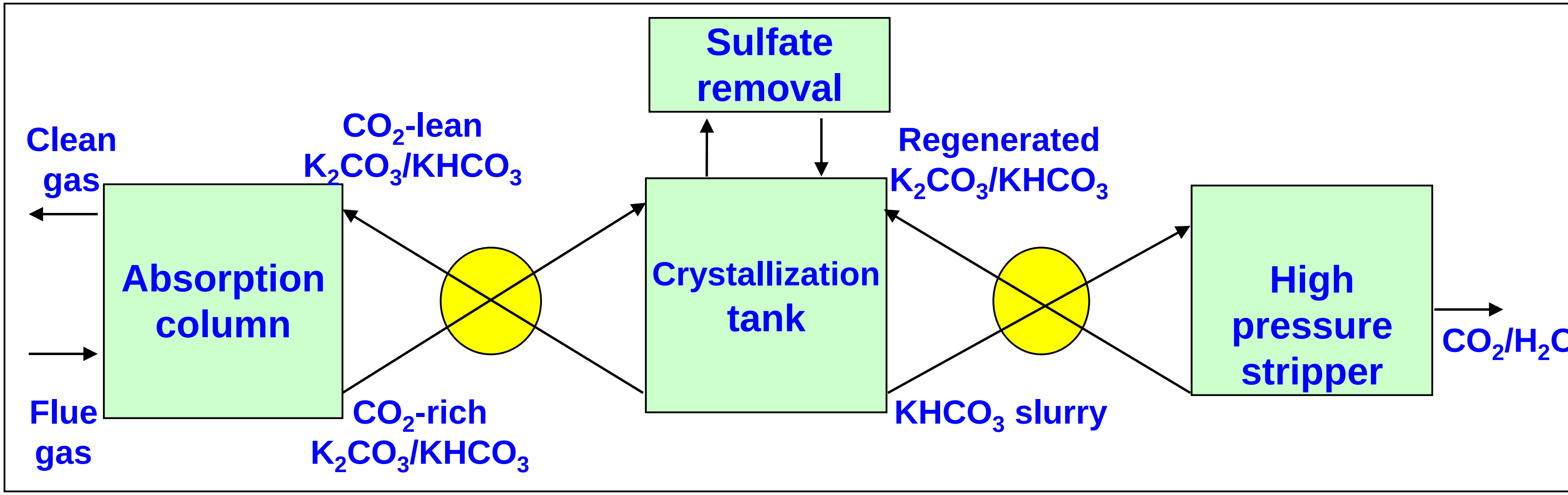
- High heat of reaction
- Low working capacity (high L/G and sensible heat)
- Low pressure stripping (high stripping heat + high compression work)

Hot Carbonate Absorption Process with High Pressure Stripping Enabled by Crystallization (Hot-CAP): Process Flow Diagram



- Absorption at 70-80 °C
- Working capacity of 40%wt (equivalent) PC: ~15-40% carbonate-to-bicarbonate conversion
- Crystallization at room temperature (~30°C)
- Stripping of bicarbonate slurry at up to ~40 atm

Major Reactions



SO_4^{2-} *reclamation*

$$K_2SO_4 + CaO + 3H_2O + 2CO_2 = 2KHCO_3 + CaSO_4 \cdot 2H_2O(s)\downarrow$$

CO_2 *absorption at* $70-80°C$

$$CO_2 + H_2O + K_2CO_3 = 2KHCO_3$$

$$SO_2 + 1/2O_2 + K_2CO_3 = K_2SO_4 + CO_2$$

Crystallization at $30°C$

$$KHCO_3 = KHCO_3(s)\downarrow$$

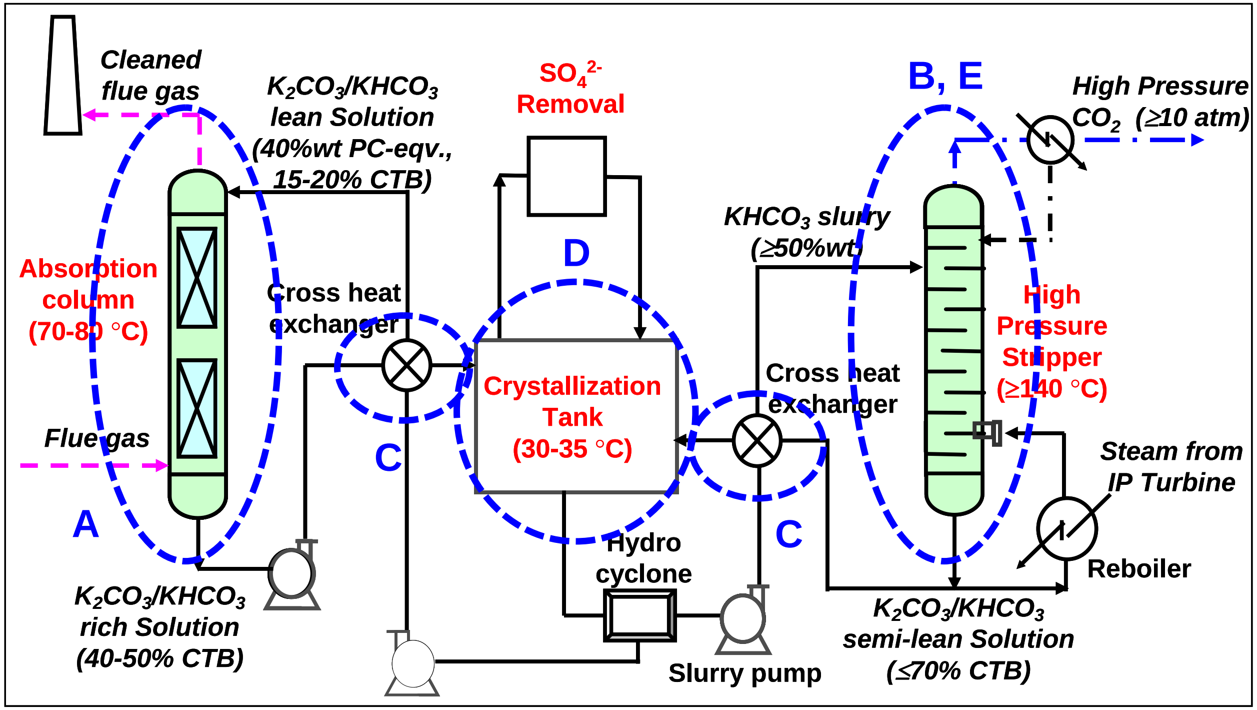
CO_2 *desorption at* $\geq 140°C$

$$KHCO_3 = CO_2(g)\uparrow + H_2O + K_2CO_3$$

Hot-CAP vs. MEA

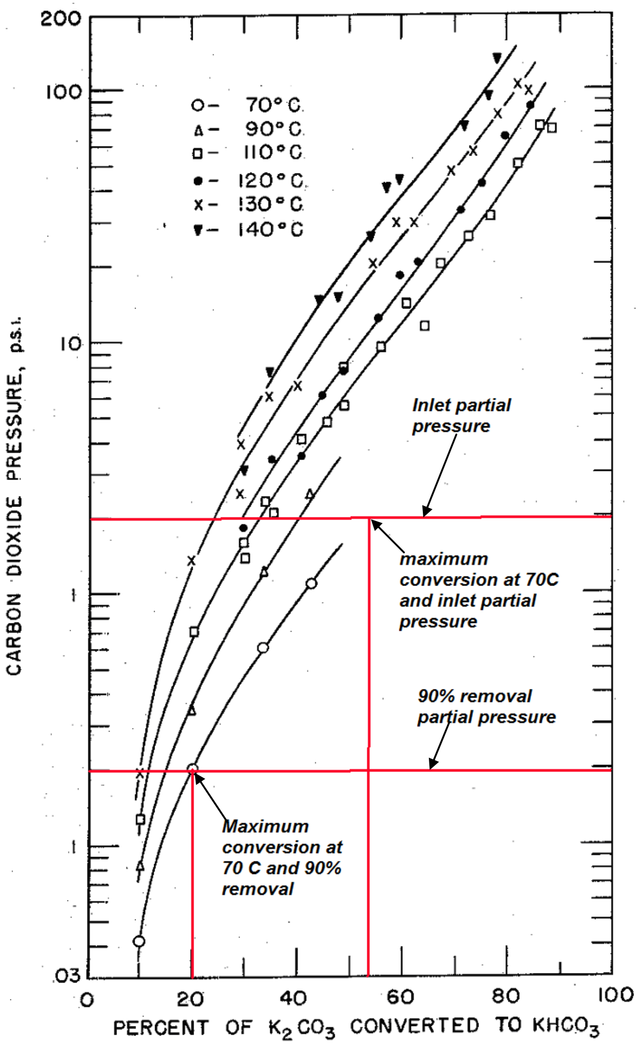
Items	MEA	Hot-CAP
Solvent	30wt% MEA	40wt% K_2CO_3
Solvent degradation	Y	N
Corrosion	Y	Insignificant
Absorption temperature	40-50 °C	70-80 °C
Stripping temperature	120 °C	140-200 °C
Stripping pressure	2 atm	8-40 atm
Phase change bw. absorb. and stripping	N	Crystallization
FGD required	Y	N

Technical Risks



Risk	Mitigation
A. Insufficient rate of CO_2 absorption	Develop promoters/catalysts & reconfigure absorption column
B. Stripping pressure not high enough (e.g.,<10 atm)	Develop a sodium bicarbonate-based slurry
C. Heat exchanger and crystallizer fouling	Vender consultation, engineering analysis and customized design
D. Insufficient cooling rate in crystallizer affects cost/space	Same as above
E. Stripper required to handle slurry and high pressure	Same as above

(a) CO_2 Absorption

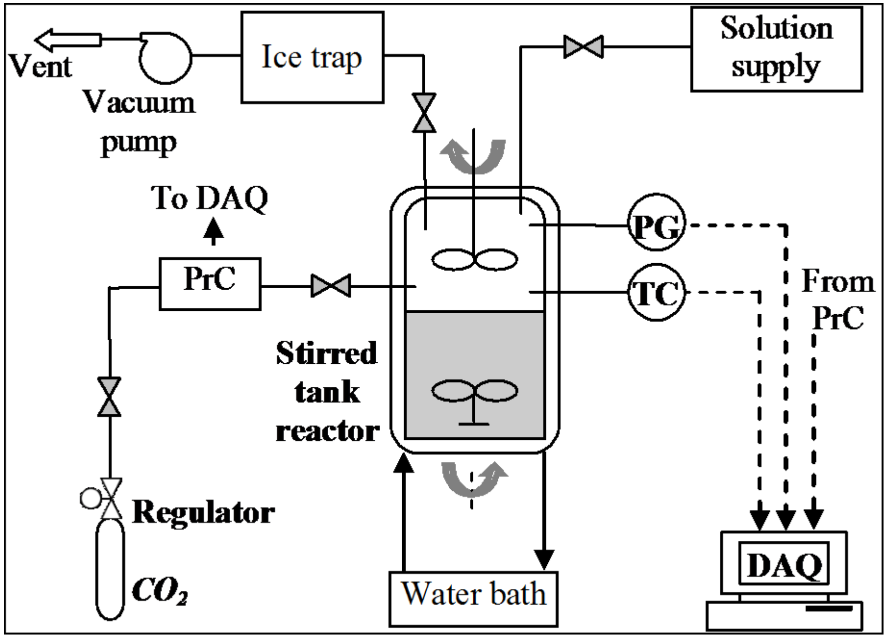


Vapor-liquid equilibrium of CO_2–K_2CO_3/$KHCO_3$ (40%wt) system

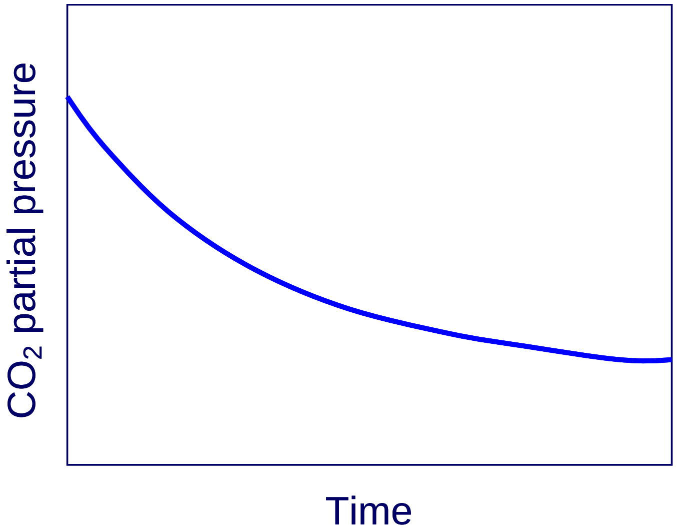
- VLE data show 90% CO_2 removal (P_{CO2}=2 -0.2 psia) is possible
  - 40%wt PC-equivalent solution
  - K_2CO_3-to-$KHCO_3$ conversion from 15-20% at inlet to 40-53% at outlet at 70-80°C

Data Source: Kohl & Nielsen. Gas Purification 5th Edition, Houston: Gulf Publishing, Houston, 1997.

Stirred Tank Reactor (STR) Experimental Setup for Absorption Tests



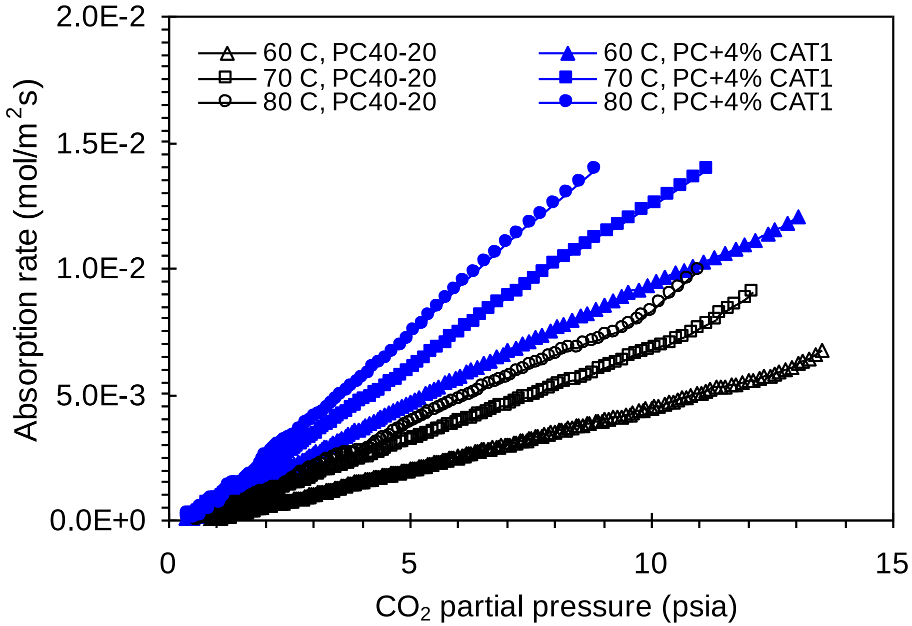
(PrC: Pressure controller; TC: Thermal couple; PG: pressure gauge DAQ: Data acquisition)

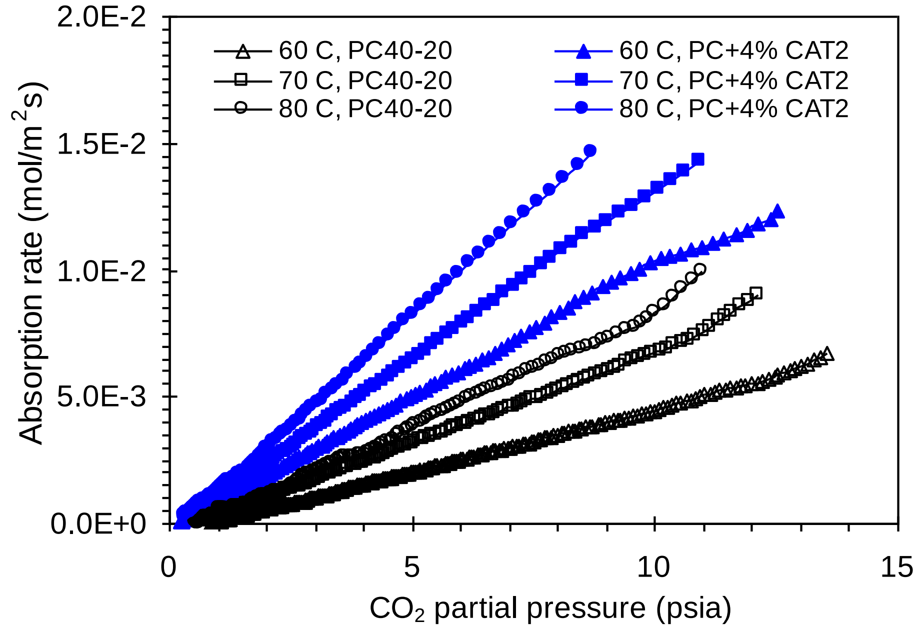


- Instant flux of CO_2 absorption

$$J_{CO2} = \frac{dP_{CO2}}{dt} \frac{V_g}{R\,T\,A_{GL}}$$

CO_2 Absorption into 40 wt% PC w/o and with Catalysts



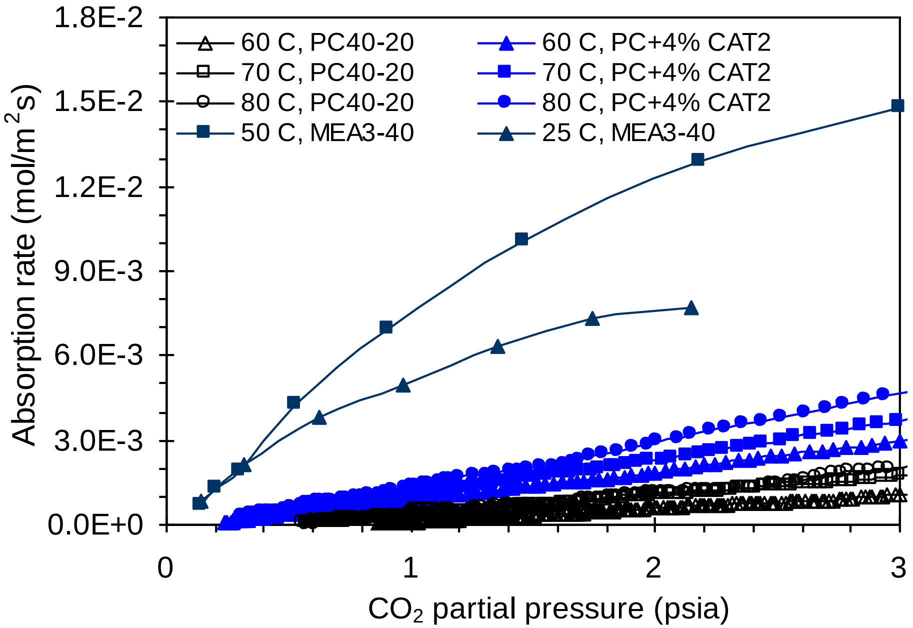


(* Rates measured in a stirred tank reactor (STR) with minimal gas phase diffusion resistance)

Enhancement factor (E)	4wt% CAT1	4wt% CAT2
E (60°C)	2.16	2.36
E (70°C)	1.86	2.00
E (80°C)	1.88	2.12

- Two inorganic catalysts, CAT1 and CAT2, identified more effective than other tested inorganic catalysts
- Addition of 4 wt% CAT1 or CAT2 raised rate by 2 times at 60, 70, 80°C

Comparison with CO_2 Absorption into MEA Solution

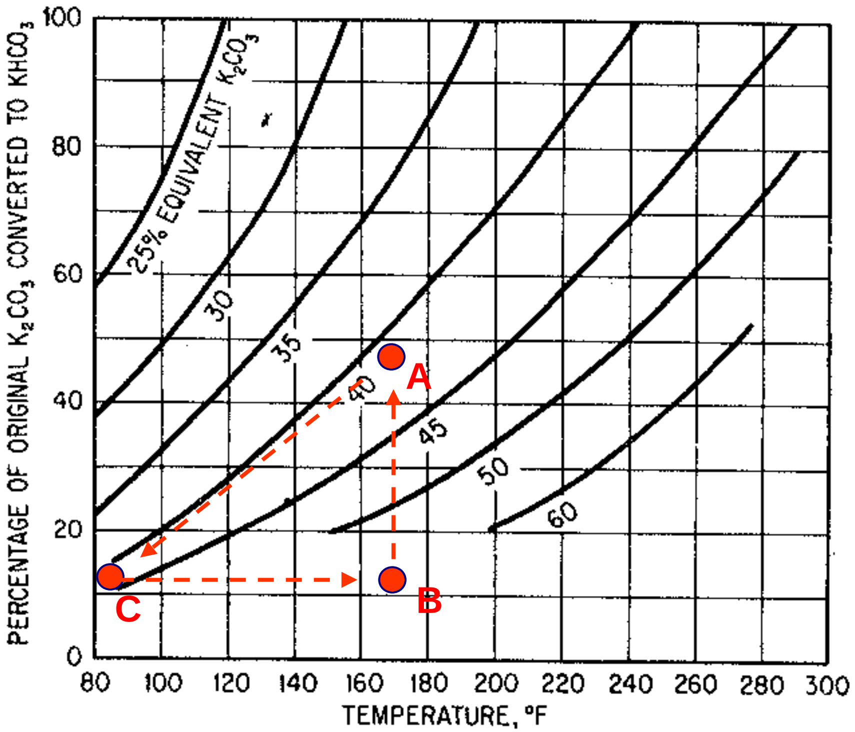


- Comparison with 3M MEA with 40% conversion (MEA3-40) at 50°C
  - STR rates into PC40-20 w/o a catalyst at 80°C were 7-18 times slower
  - Rates into PC40-20 with CAT2 at 80°C were 3-5 times slower

- Rate difference between MEA and PC40 is smaller in a packed-bed column than a STR because of the significant effect of gas phase diffusion for the MEA in a packed bed

(b) Bicarbonate Crystallization

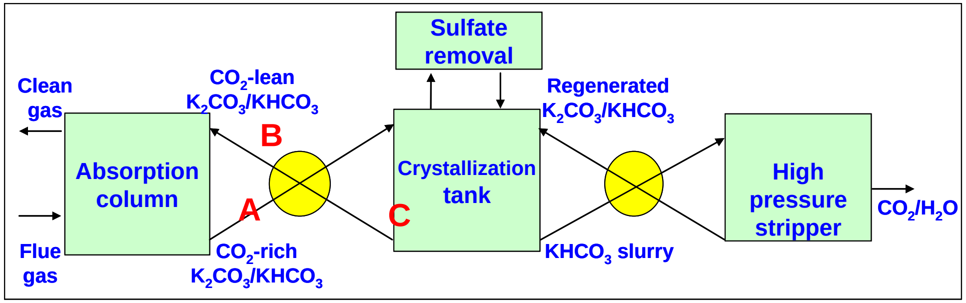
- Bicarbonate will crystallize from A to C when cooled to 30°C
- Crystallization not occurring in absorption column (B to A)



A: at the bottom of absorption column

C: Crystallizer

B: at the top of absorption column (equiv. to C heated to 70-80°C



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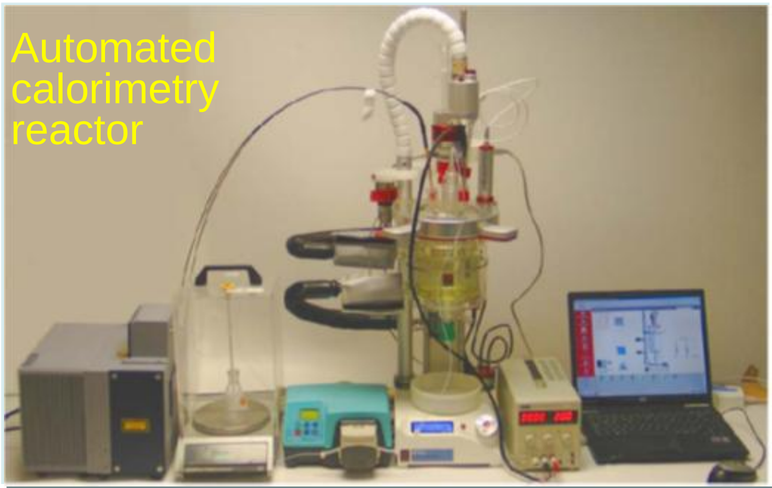
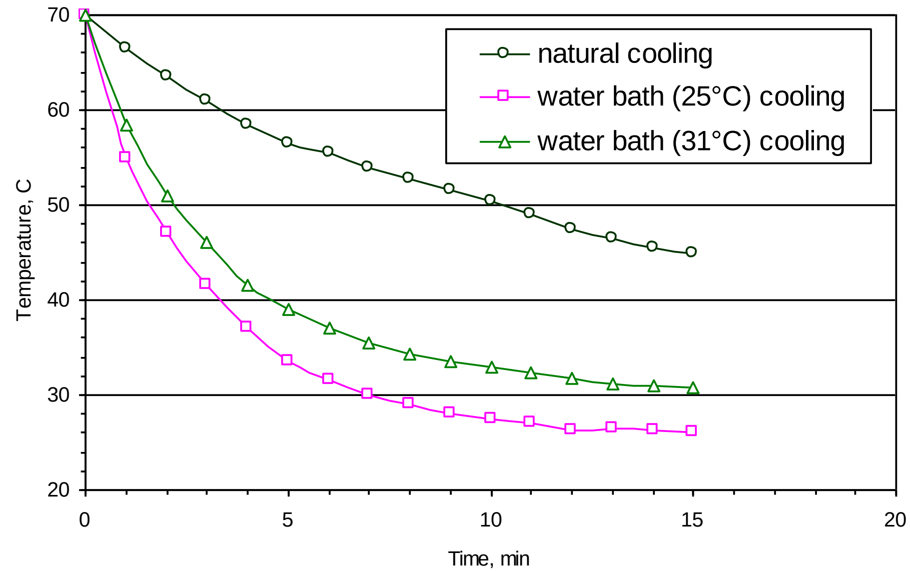
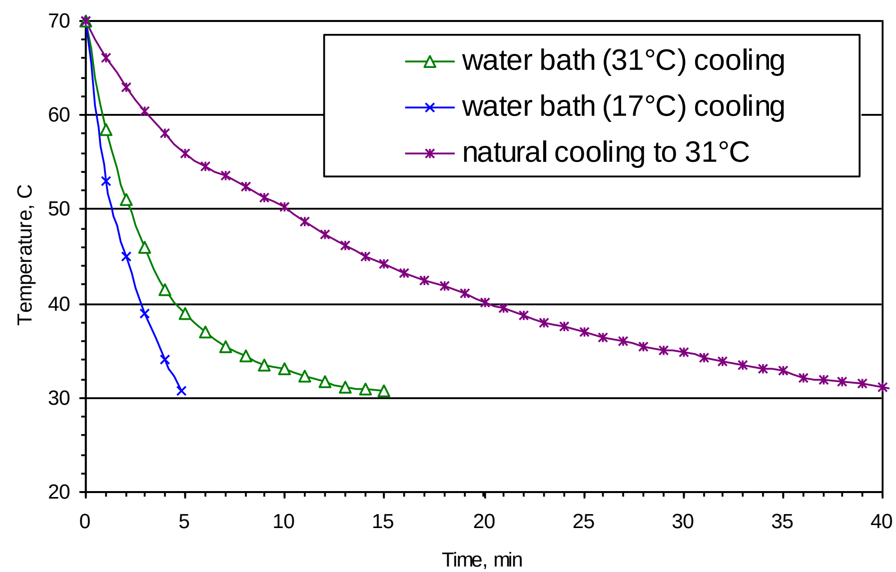
Kinetic Feasibility of Bicarbonate Crystallization

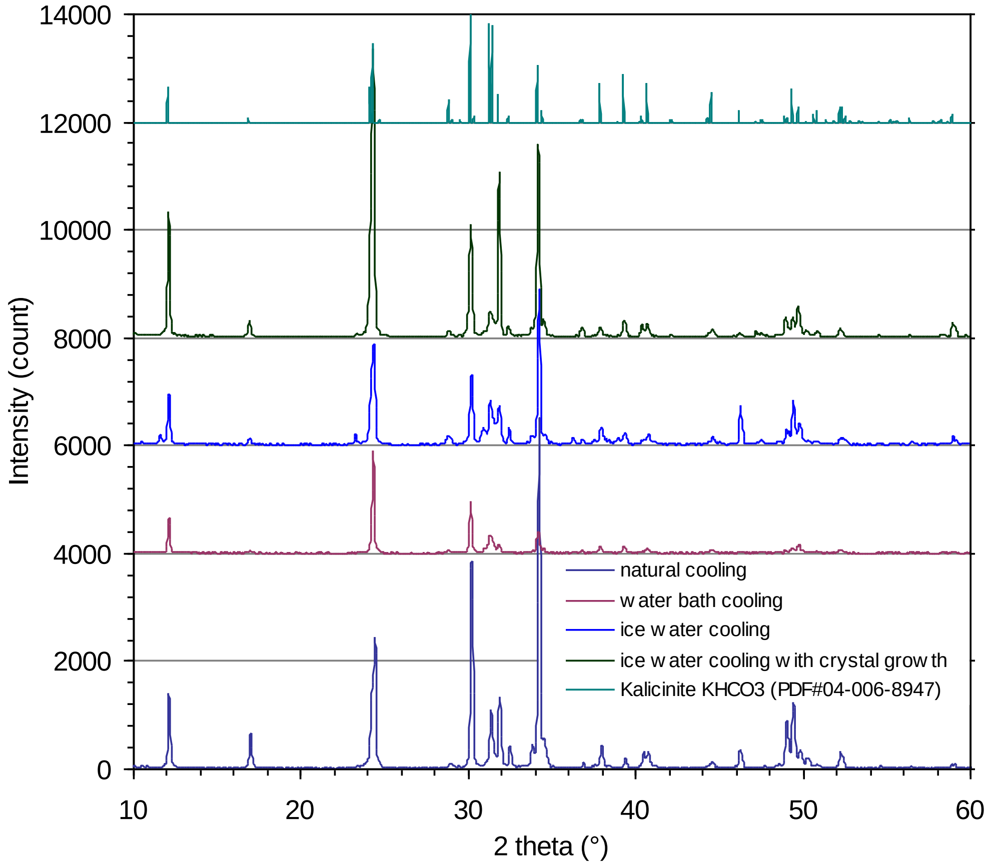


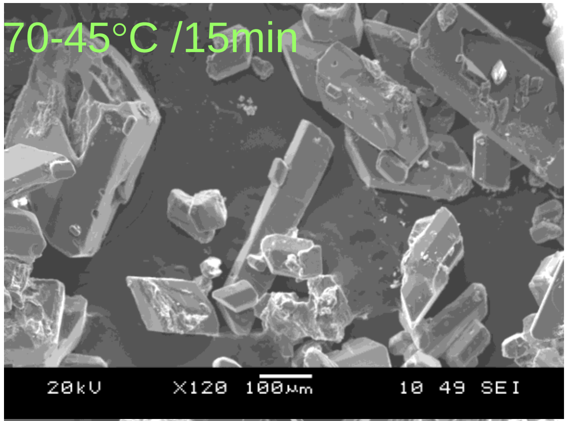


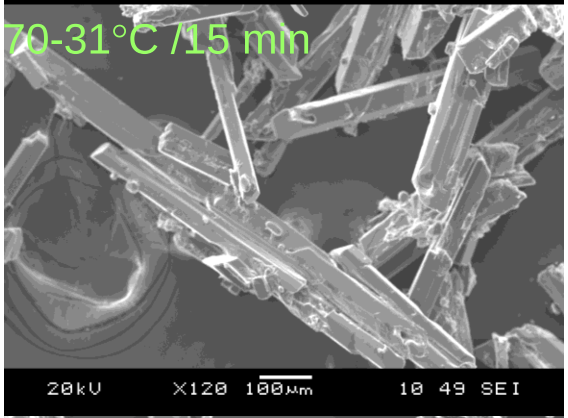


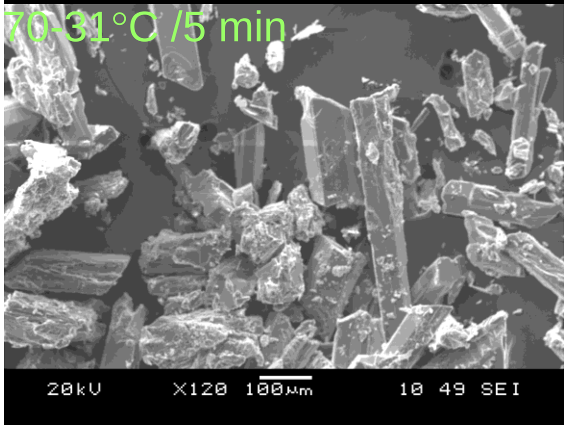
- 40wt% PC solution with 40% conversion (PC40-40) employed
- Starting T=70°C to end T=25-45°C
- Rate of crystallization controlled by cooling rate
  - Crystals formed immediately with decreasing T and preceded continuously
  - In rapid cooling, rate could be limited by nucleation

Analysis of Crystal Products





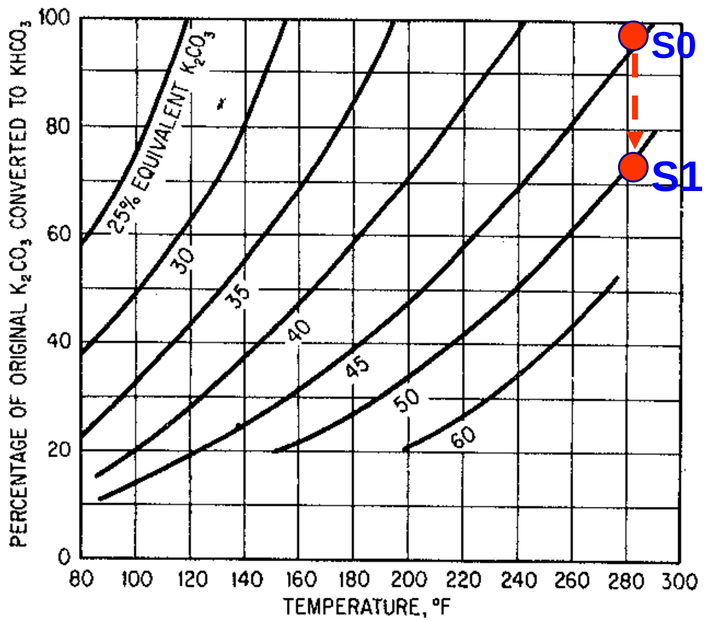




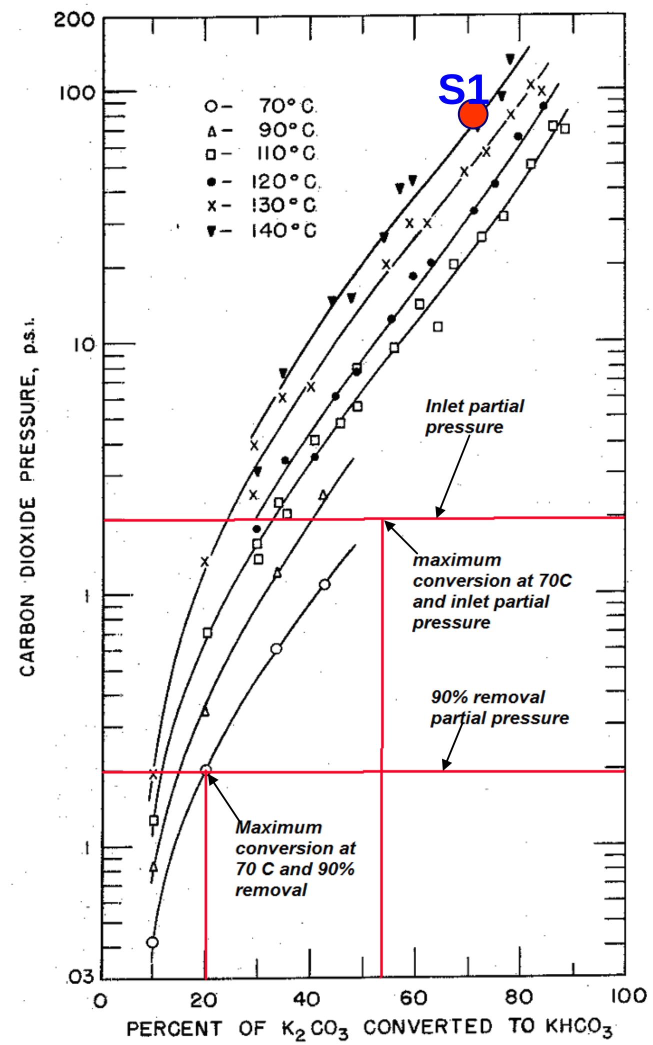
- High purity kalicinite ($KHCO_3$) prevailed in products
- More needle-shape crystals at lower cooling rate
- Small deposits on crystal surface at faster cooling
- Yield of $KHCO_3$ crystals (~50%) determined by end T

(c) High Pressure Stripping

- Assuming ~50%wt slurry, 30% change of K_2CO_3-to-$KHCO_3$ conversion (100%-70%), 140 °C
  - Working capacity of PC in stripper similar to MEA but C_p =~1/2 of MEA
  - 5-10 atm CO_2 partial pressure
- Higher stripping pressure (20-40 atm) possible at higher T, higher concentration of slurry, and higher K_2CO_3-to-$KHCO_3$ conversion in solution



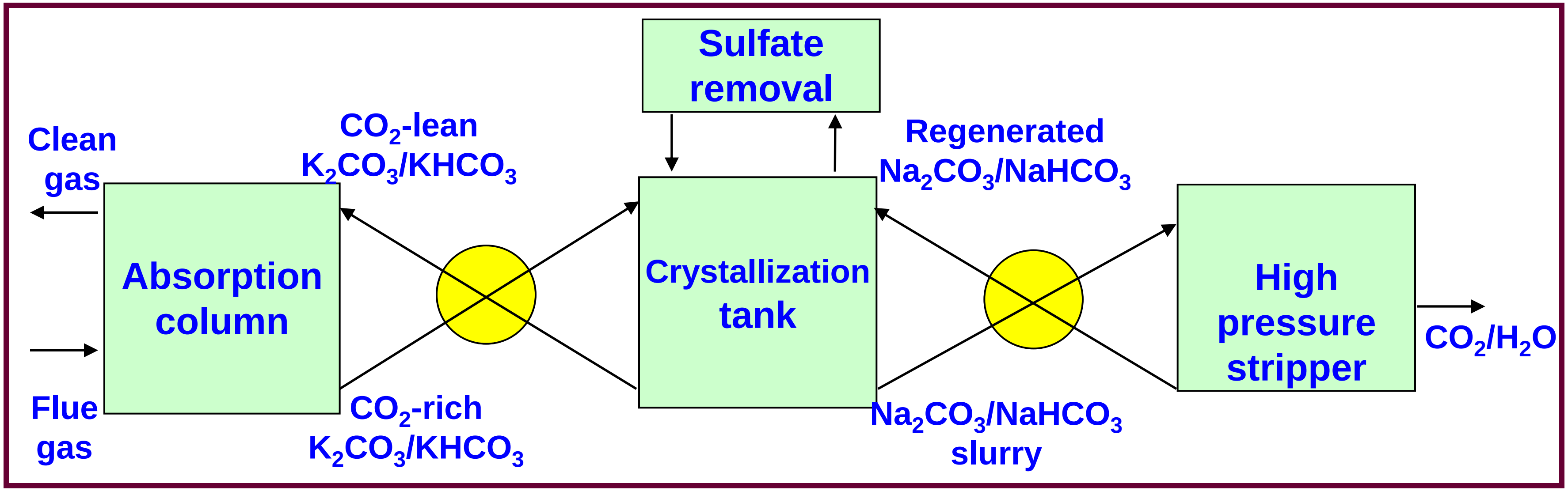
Solubility of bicarbonate in carbonate solution



Vapor-liquid equilibrium of CO_2–K_2CO_3/$KHCO_3$ (40%wt) system

Technical Option to Further Increase Stripping Pressure

- Stripping pressure could be further increased by using $Na_2CO_3/NaHCO_3$ slurry for CO_2 desorption
  - Solubility of $NaHCO_3$ is ~half of $KHCO_3$
  - Equilibrium pressure of CO_2- $Na_2CO_3/NaHCO_3$ is higher



$$Crystallization\ at\ 30°C$$

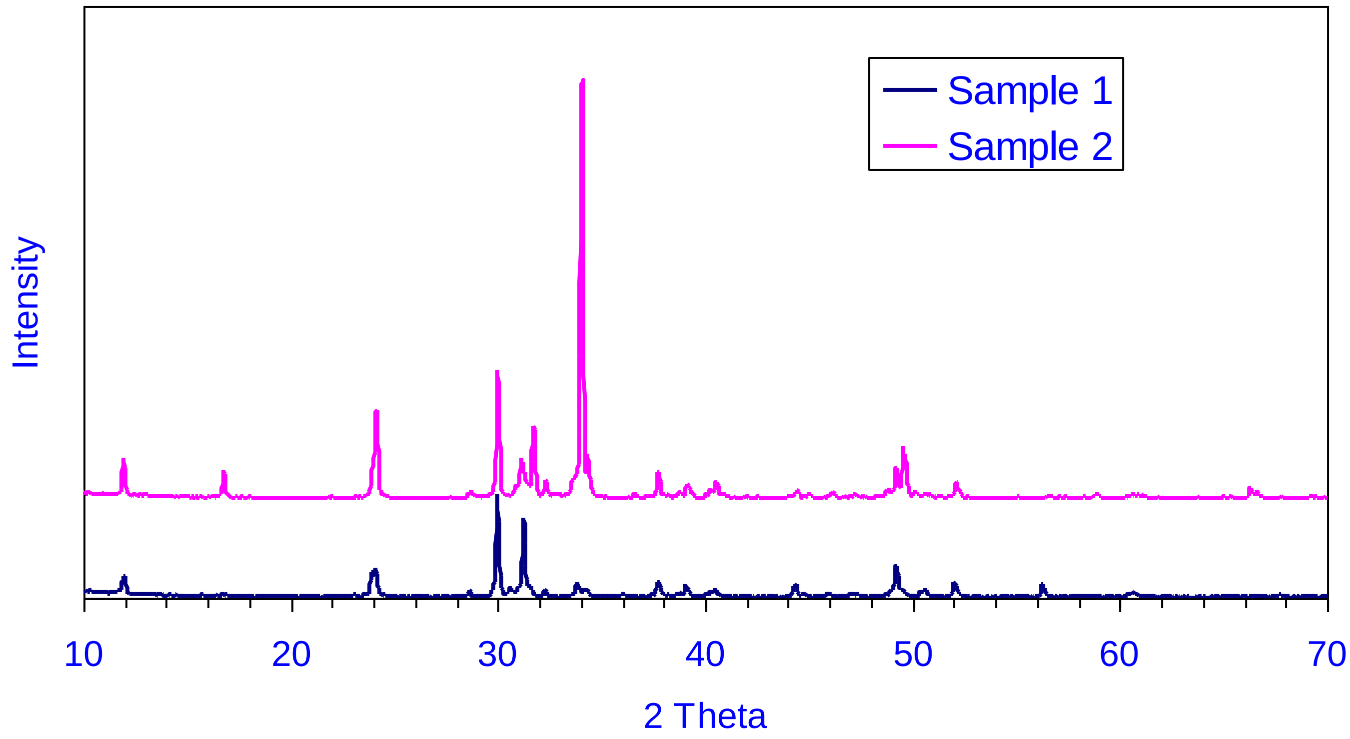
$$KHCO_3 + Na_2CO_3 = NaHCO_3(s)\downarrow + K_2CO_3$$

$$CO_2\ desorption\ at \geq 140°C$$

$$NaHCO_3 = CO_2(g)\uparrow + H_2O + Na_2CO_3$$

Competitive Crystallization between $NaHCO_3$ and $KHCO_3$

- XRD result indicates $NaHCO_3$ can precipitate from $KHCO_3$+Na_2CO_3 system



Sample1 = 40%wt PC with 40% conversion, cooling from 75-25 °C
Sample2 = 40%wt PC with 40% conversion + 10%wt Na_2CO_3, cooling from 75-25 °C

Advantages of Hot-CAP

- High stripping pressure
  - Low compression work
  - Low stripping heat (high CO_2/H_2O ratio)
- Low sensible heat
  - Comparable working capacity to MEA
  - Low Cp (1/2)
- Low heat of absorption
  - 7-17 kcal/mol CO_2 (crystallization heat incld.) vs. 21 kcal/mol for MEA
- FGD may not be required
- No solvent degradation
- Lower cost than amines
- Less corrosive than amines

Energy Use Comparison bw. Hot-CAP and MEA

Items	MEA	Hot-CAP
Energy Consumption		
CO_2 desorption		
Heat of absorption (Btu/lbCO_2)	825	600
Sensible heat (Btu/lbCO_2)	600	300
Stripping heat (Btu/lbCO_2)	270	30
Electricity equivalent (kWh/ kg CO_2)	0.23 (based on 120°C steam)	0.17 (based on 140-200°C steam)
Compression work (kWh/ kg CO_2)	0.10	0.03
Total electricity (kWh/kg CO_2)	0.33	0.20
Operating		
Degradation (kg MEA/ ton CO_2)	2	0
FGD Required	Y	N

Hot-CAP system projected to have overall 40% less parasitic power than benchmark MEA system

Summaries

- Hot-CAP can achieve 90% CO_2 removal
- Parasitic power loss reduced by ~40% compared to MEA
- Crystallization in absorption column is prevented
- Absorption is decoupled from desorption, but to reduce absorber size, an effective absorption promoter/catalyst is required
- Crystallization process is fast and rate is controlled by cooling rate

- Ongoing and future work activities
  - Screening tests of absorption promoters/catalysts
  - Bench-scale absorption and high-pressure stripping column tests
  - Risk mitigation studies

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